Principles and fundamentals of x-ray absorption fine structure in actinides

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- Provides:
  - radial bond length distribution from absorbing atom's point of view
  - some electronic configuration information
- Fundamental problems:
  - speciation
  - association
  - local vs. average structure
  - vibrational properties

- Advantages
  - does not depend on long-range (crystallographic) order
  - atomic species specific
  - can probe very low concentrations (legends of µM…)
  - typically uses hard x-rays, so is a bulk probe
  - user synchrotron facilities such as SSRL and ALS
- Disadvantages
  - very short range (< ~ 5 Å)
  - using low Z < ~ Ca difficult

Actinides and acetates
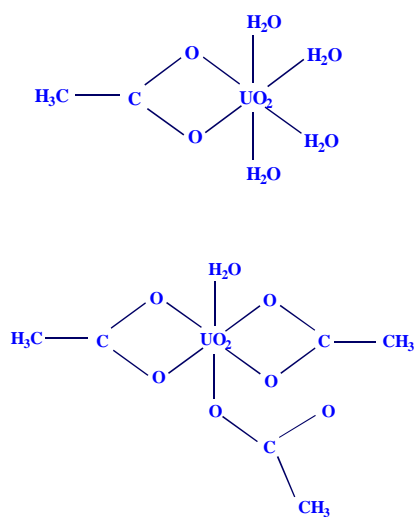
- Example of basic solution chemistry coupled with EXAFS.
- Organic complexation of uranyl ligands in tank wastes is still poorly understood
- Searching for thermodynamic and XAFS signatures to determine ligation.

- Experiment: identify stable acetate species in given solutions, try to draw conclusions from changes in entropy/enthalpy with regard to ligation.
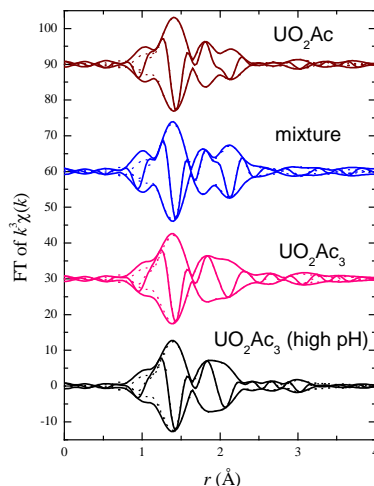
Thermodynamic simulation

XAFS results

$[UO_2(CH_3COO)^b(H_2O)_4]^+$
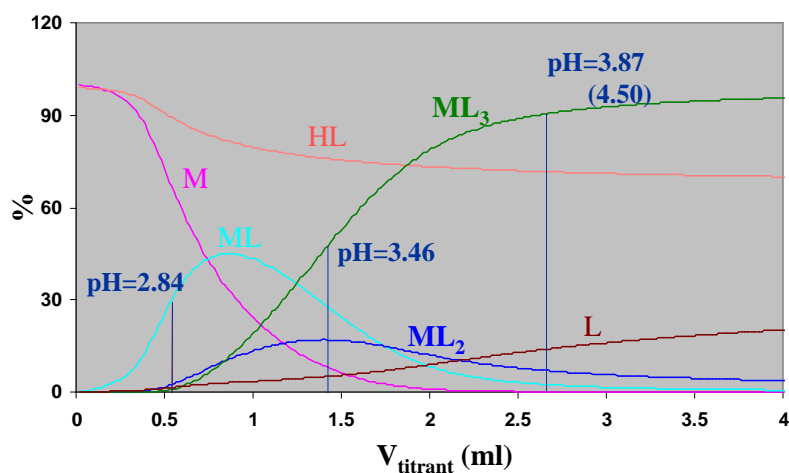
Atom	R (Å)	σ	N
O	1.78	0.0411	2.0
O	2.38	0.0703	4.0
O	2.50	0.0920	2.0
C	2.91	0.0500	1.3

$[UO_2(CH_3COO)^b_2(CH_3COO)^m(H_2O)]^-$

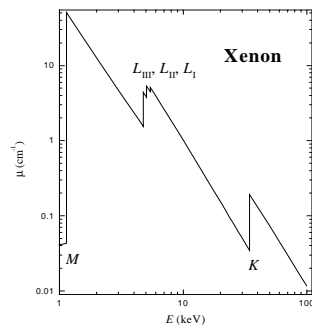| Atom	R (Å)	σ	N
O	1.78	0.0344	2.0
O	2.34	0.0533	1.9
O	2.48	0.0482	4.1
C	2.87	0.0500	2.1

J. Jiang, L. Rao, C. Booth

## X-ray and XAFS history

1895   x-rays discovered by W. Roentgen (Nobel 1901)

1907   "Characteristic" x-rays discovered by C. G. Barklin (Nobel 1917)

1912   Diffraction, M. von Laue (Nobel 1914)

1913   Verification of Bohr's model using characteristic x-rays (K, L spectra)

1922   Elastic (Thompson, coherent) vs. Inelastic (Compton, incoherent) scattering, A. Compton

1931   extended x-ray absorption fine structure recognized, initial attempts at explanation, Kronig

1941   Essentially correct theory, field still confused by Kronig's meanderings, Kosterev

1960's   F. Lytle starts experimenting with XAFS at Boeing, E. Stern get's involved, along with his graduate student D. Sayers

1971   Sayers, Stern and Lytle published in PRL, stop the confusion, open up the field of local structure spectroscopy

1974   SSRP (later SSRL) opened the synchrotron radiation era!
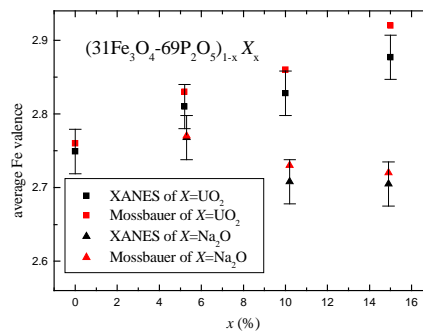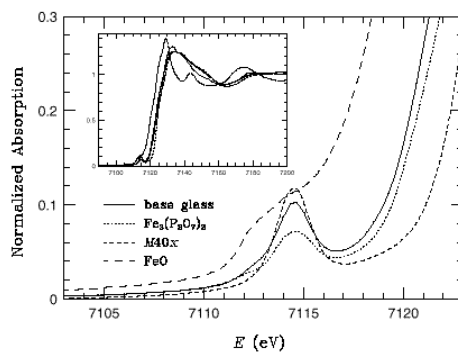
X-ray absorption spectroscopy

Xenon

L_{III}, L_{II}, L_{I}

μ (cm^{-1})

M

K

E (keV)

From McMaster Tables

continuum

E_F

filled 3d

γ

1s

core hole
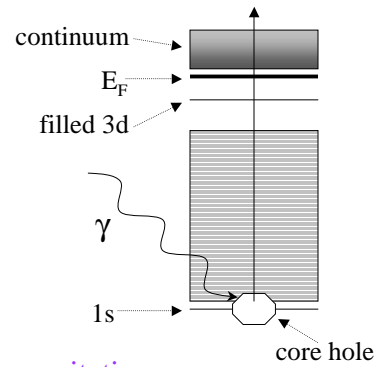
- Main features are single-electron excitations.
- Away from edges, energy dependence fits a power law: $\mu \propto AE^{-3} + BE^{-4}$ (Victoreen).
- Threshold energies increase roughly as Z^2.

X-ray absorption near-edge structure (XANES)

Normalized Absorption

base glass
$Fe_3(P_3O_7)_3$
M40x
FeO

E (eV)

$(31Fe_3O_4\text{-}69P_2O_5)_{1-x} X_x$

average Fe valence

■ XANES of X=UO$_2$
■ Mossbauer of X=UO$_2$
▲ XANES of X=Na$_2$O
▲ Mossbauer of X=Na$_2$O

x (%)

Often can measure valence by looking at threshold energy shifts

Requires that local configuration is NOT changing much…

Discovery of x-ray absorption fine structure
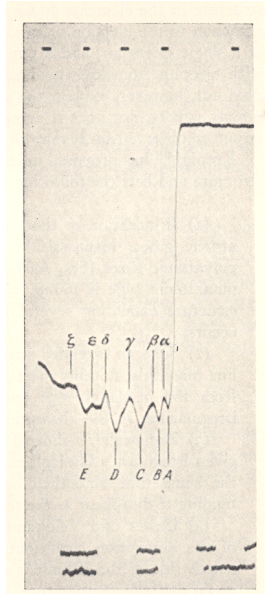
- First noticed before 1920
- Many hair-brained (sort-of) explanations…
- Closest by Kronig (Z. Phys. 70, 317, 1931; 75, 191,1932; 75, 468, 1932)
- LRO (crystals) utilized gaps (actually a 2nd-order effect)
- SRO (molecules) utilized backscattering photoelectrons

Coster and Veldkamp, Z. Phys. 70, 306 (1931). See also X-Rays in Theory and Experiment (1935), by Compton and Allison, p. 663.
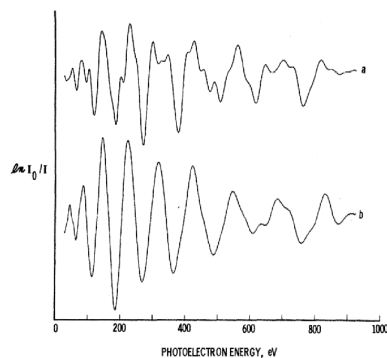

The dawn of a new age…

FIG. 1. Smoothed experimental EXAFS data for (a) crystalline and (b) amorphous Ge. Only the oscillatory part χ of the absorption edge is shown.
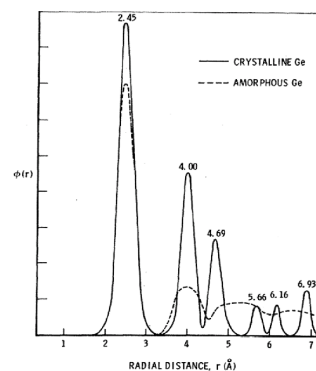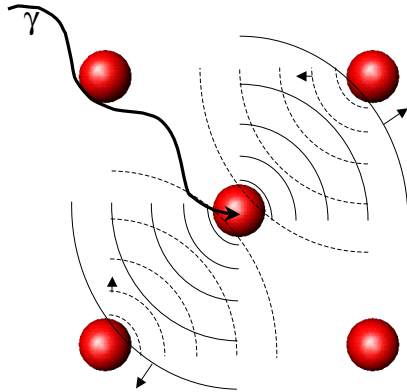
FIG. 2. Fourier transformation of the data of Fig. 1. $\varphi(r)$, a radial structure function, compares amorphous and crystalline Ge. Numbers over the peaks indicate the measured distances in Å.

$$\chi(k) \propto N \sin(2kr + \phi)$$

Sayer, Stern and Lytle, *Phys. Rev. Lett.* **71**, 1204 (1971)

Interference of photoelectron waves

γ

"I was brought up to look at the atom as a nice hard fellow, red or grey in colour according to taste."

- Lord Rutherford

- Interference of outgoing and incoming part of photoelectron modulates absorption coefficient:

$$\mu \propto \left| \left\langle f \left| \varepsilon \cdot r \right| i \right\rangle \right|^2$$

$$\mu = \mu_0 (1 + \chi(k))$$

$$\chi(k) \propto \sum_i N_i \int g(r) \sin(2kr + \phi_{ci}) dr$$

g is a radial pair - distribution function

- <u>Big advantage</u>: Atomic-species specific.
- *Disadvantages*: very short range (<~5-6 Å), sensitive to multiple scattering, overlapping edges...

EXAFS

"white line"

UCu₄Pd

Normalized Absorption

U L_{III} edge

E (eV)

STANFORD SYNCHROTRON RADIATION LABORATORY

SSRL
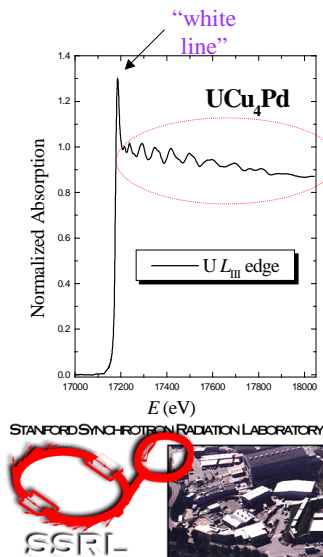
- Oscillatory structure above the main edge is called the "extended x-ray-absorption fine-structure", or EXAFS

- Other excitations are possible... the "white line" in L_{III}-edge absorption is often due to $2p \rightarrow d$ transitions:

continuum

E_F

partially filled 3d

γ

2p

core hole
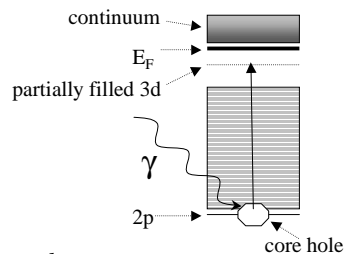
"*In one trip to the synchrotron we collected more and better data in three days than in the previous ten years.*"
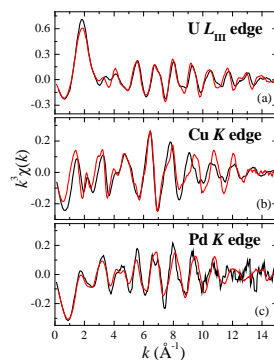– Farrell Lytle

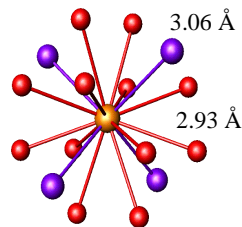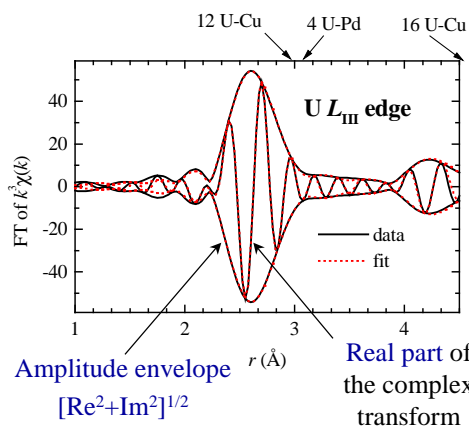# X-ray absorption spectroscopy (XAS) experimental setup
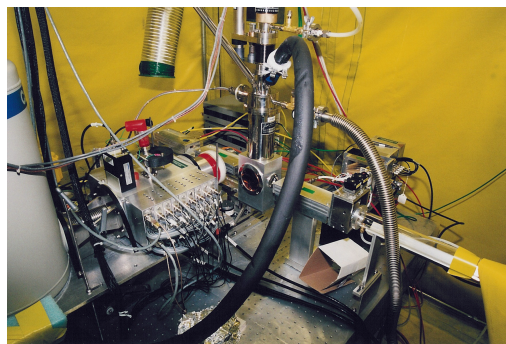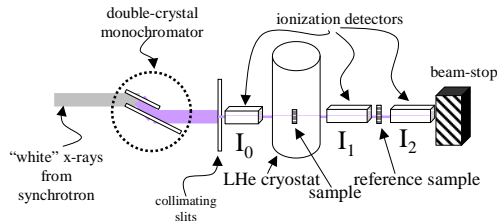
- sample absorption is given by
  $$\mu\, t = \log_e(I_1/I_0)$$
- reference absorption is
  $$\mu_{REF}\, t = \log_e(I_2/I_1)$$
- EXAFS $\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k)$
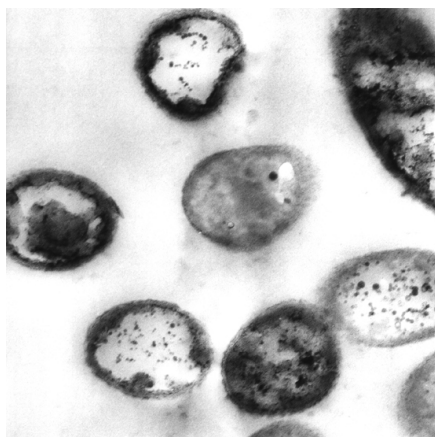

How to read an XAFS spectrum

$$\chi(k) \propto \sum_i N_i \int g(r) F(k,r) \sin(2kr + \phi_{ci})\, dr$$

g is a radial pair-distribution function

- **Peak width depends on back-scattering amplitude *F(k,r)* , the Fourier transform (FT) range, and the distribution width of *g(r)*, a.k.a. the Debye-Waller s.**
- **Do NOT read this strictly as a radial-distribution function! Must do detailed FITS!**
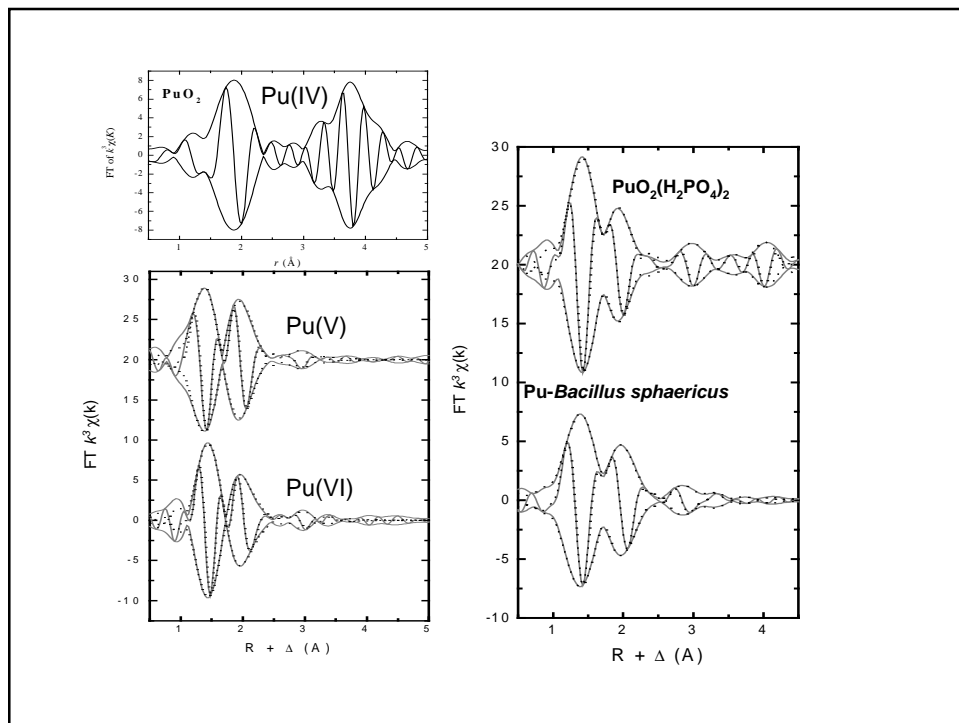
Actinides in bacteria

- possibility exists for certain bacteria to express phosphate
- These phosphates may complex with UO_2^{2+} under aerobic conditions.
- "Converting" UO_2^{2+} into a phosphate is beneficial because U-phosphates are less soluble than uranyl.
- A procedure exists to remove such actinides from a solution…

Actinides are a little bit different…
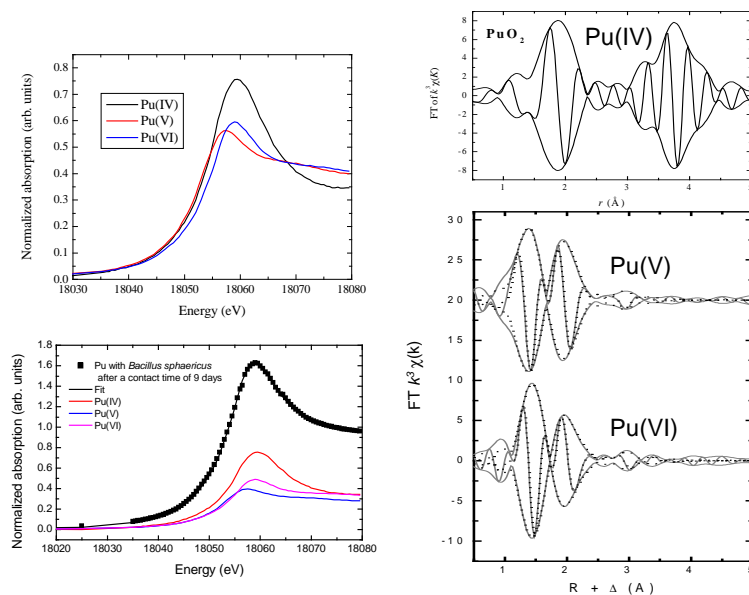
XAFS of uranium-bacterial samples
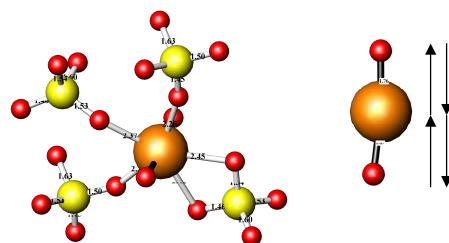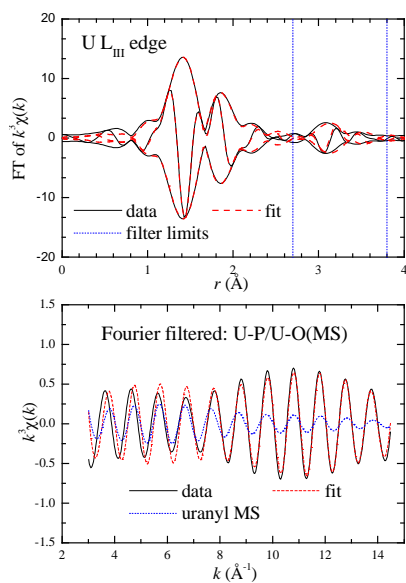
- XAFS can tell us whether uranium and phosphate form a complex
- U-phosphate is less soluble than UO_2^{2+}, amenable to anaerobic cleansing.
- Fits indicate both monodentate coordination to phosphorous, and bidentate coordination to something else (probably carbon).

Panak, Booth, Nitsche, LBNL

Further reading

Sir Lawrence Bragg, The Development of X-ray Analysis (Dover)

Farrel W. Lytle, "The EXAFS family tree: a personal history of the development of extended X-ray absorption fine structure," J. Synchrotron Rad. **6**, 123 (1999).

Edward A. Stern, "Musings about the development of XAFS," J. Synchrotron Rad. **8**, 49 (2001).

Boon K. Teo, EXAFS: Basic Principles and Data Analysis (Springer-Verlag).

D. Konigsberger and R. Prins (ed.) X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES (Wiley).

J. J. Rehr and R. C. Albers, "Theoretical approaches to x-ray absorption fine structure," Rev. Mod. Phys. **72**, 621 (2000).